International Journal Of Advancement In Engineering Technology, Management and Applied Science (IJAETMAS)
ISSN: 2349-3224 || www.ijaetmas.com || Volume 03 - Issue 07 || July 2016 || PP. 52-55

Synthesis of Photoconducting Co-polymer of 2- Methacryloyl -1- (4- azo- 1' –phenyl) phenolWith Styrene.

Dipak Kumar Mukhopadhyay
Institute of Science & Technology, C.K Town, West Bengal, 721201, India

ABSTRACT :

The azo dye namely 4- hydroxyazobenzene has been synthesized and the corresponding monomer 2-methacryloyl – 1- (4-azo -1'- phenyl) phenol has been synthesized by the reaction of azo dye namely 4-hydroxyazobenzene with methacryloyl chloride . Then the Corresponding Co-polymer of 2- methacryloyl -1-(4-azo- 1'-phenyl) phenol with styrene has been synthesized. The monomer and the corresponding Co-polymer have been characterized by UV, Visible and NMR spectroscopy.

Key Words:*4- hydroxyazo benzene,Methacryloyl chloride, 2 – methacryloyl-1- (4 –azo -1' –phenyl) phenol, solution polymerization.*

I. INTRODUCTION :

Photoconducting polymers are the subject of intense study owing to their potential applications in photorefractive devices, light emitting diodes, photovoltaic and many other optoelectronic devices. The possibility of adjusting the properties by modifying the structure is the attractive feature of polymeric systems. Photoconductivity in polymeric systems is a complex process involving absorption of radiation, generation of charge carriers, injection,transport,recombination and trapping.

One of the necessary requirements for photorefractivity is photoconductivity .The polymeric photoconductor used in practise are based on two type of systems. In the first, the charge transporting unit is a part of the polymer chain and in the second, low molecular weight charge generating and charge transporting molecules are embedded in a polymeric matrix. These are called molecularly doped polymers. A large number of polymers with charge –transporting units in the side chain and main chain, polymers with Pi- conjugated and sigma-conjugated main chain were extensively studied. Different classes of photoconductingpolymers have discussed elsewhere. Molecularly doped systems have attracted great attention because of their importance in the construction of transport theories in amorphous photoconductors. The main drawback with these systems is phase separation due to presence of large number of low molecular dopants in the inert polymer host matrix. Hence the application of molecular doping towards stable photorefractive polymer systemis limited. In order to decrease the chances of phase separation, polymers were synthesized with charge transporting units chemically attached to the main chain or as side chain. Most of the photorefractive systems studied to date consist of charge transporting polymers as host for a wide variety of electro-optic chromophores.

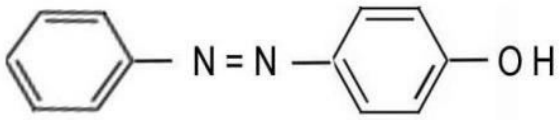
In this section photoconducting and non-conjugated copolymer of 2- methaeryloyl -1 – (4-azo-1'-phenyl) phenol with styrene has been synthesized.

II. EXPERIMENTAL:

2.1 Synthesis of 4 – hydroxyazobenzene:

At 0^0c, 27 g (0.29mol)of aniline were dissolved with vigorous stirring in 125 g of 27% hydrochloric acid. Afterwards, at 0^0-5^0c, 23.8 g (0.345 mol)of sodium nitrite (dissolved in 70 ml of water) were added dropwise and the solution was stirred for another 60 minutes on completion of addition .Excess sodium nitrite was destroyed with amidosulphuric acid .In a further flask 18.8 g (0.2 mol) of phenol were dissolved in a solution of 45.7 g (1.14 mol) of sodium hydroxide in 570 ml of water and precooled at 5^0c . The above freshly prepared diazonium salt solution was added to this solution at such a rate that the internal temperature did not rise above 5^0c. During the addition, the P^H was monitored regularly. On completion of addition, the mixture was allowed to warm to room temperature, and stirred for a further 60 minutes, and the suspension was then adjusted to P^H= 4 using 2 (N) hydrochloric acid . The product was filtered off and wasedrepeatedly with water. After drying in a vacuum, the desired orange-brown azo compound wereobtained. The azo dye was characterized by IR, UV and NMR spectra.

International Journal Of Advancement In Engineering Technology, Management and Applied Science (IJAETMAS)
ISSN: 2349-3224 || www.ijaetmas.com || Volume 03 - Issue 07 || July 2016 || PP. 52-55



2.2 Synthesis of 2- Methacryloyl -1- (4-azo -1'- phenyl) phenol:

4- hydroxy azo benzene (3.96 g, 20 m mol) was dissolved in 50 ml dry THF under nitrogen. To the solution, pyridine (0.2 g, 2.52 m mol) and methacryloyl chloride (2 ml, 10.26 m mol) were added dropwise simultaneously. The reaction was carried out at 0^0c with magnetic stirring for 3 h and then at room temperature for 50 h .The resulting mixture was washed with hydrochloric acid (0.1 M), sodium carbonate (5%) and finally with distilled water .The excess solvent was evaporated under reduced pressure. The organic layer was dried over anhydrous sodium sulphate. The reaction product obtained was purified by column chromatography using methylene dichloride. The monomer was characterized by IR, UV, and NMR spectra.

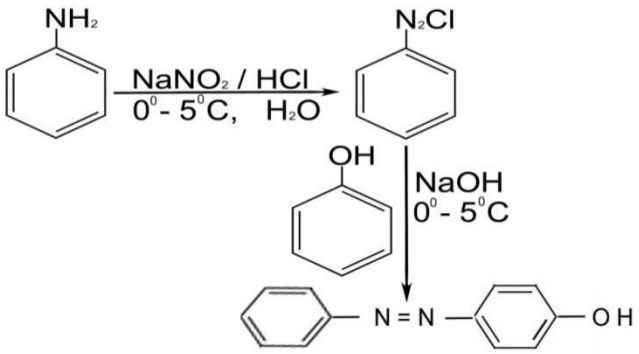
2.3 Polymerization:

2- methacryloyl-1- (4-azo-1'-phenyl) phenol (1 g, 3.77 m mol), styrene (0.39 g, 3.75 m mol) and azobisisobutyronitrile (2g, 12.19 m mol) were dissolved in dry DMF (40 ML). The reaction was carried out at 110^0c for 75h, under nitrogen. The resulting solid was dissolved in DMF and reprecipitated from methanol. Polymer was collected by filtration, dried under vacumn and stored.

III. RESULT AND DISCUSSION:

Poly (2-methacryloyl-1- (4-azo-1'-phenyl) phenol-co-styrene, comes under the class of polymer with side chain electronically isolated photo-conducting groups. It is a copolymer of 2-methacryloyl-1- (4-azo-1'-phenyl) phenol and styrene. The polymer was synthesized via radical initiated polymerization of 2-methacryloyl-1- (4-azo-1'-phenyl) phenol and styrene using solution polymerization technique.

The first monomer 4-hydroxy azo benzene was prepared at first by diazotising aniline with sodium nitrite and hydrochloric acid and 0^0-5^0c and then the diazonium salt was treated with phenol in alkaline medium at 0^0-5^0c.The synthesis route of 4-hydroxy azo benzene given in Scheme – I.

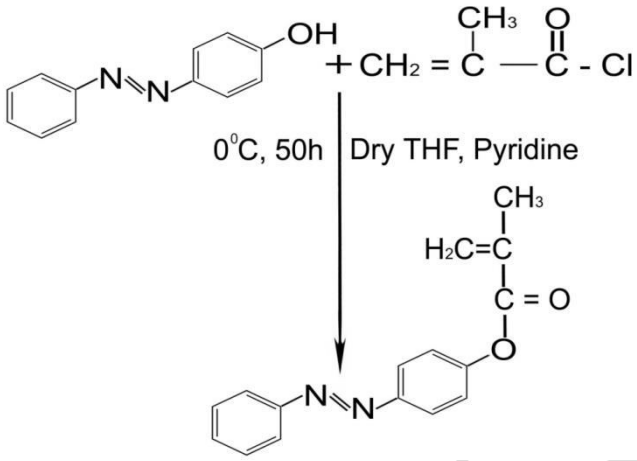


Scheme – I

The second monomer 2-methacryloyl-1- (4-azo-1'-phenyl) phenol was synthesized by reacting 4-hydroxy azo benzene with methacryloyl chloride. The two monomers were obtained in acceptable yields. The monomers have good solubility in common organic solvents like THF, DMF, acetone, chloroform .The structure of monomers were confirmed by FT-IR, NMR and mass spectral analysis.

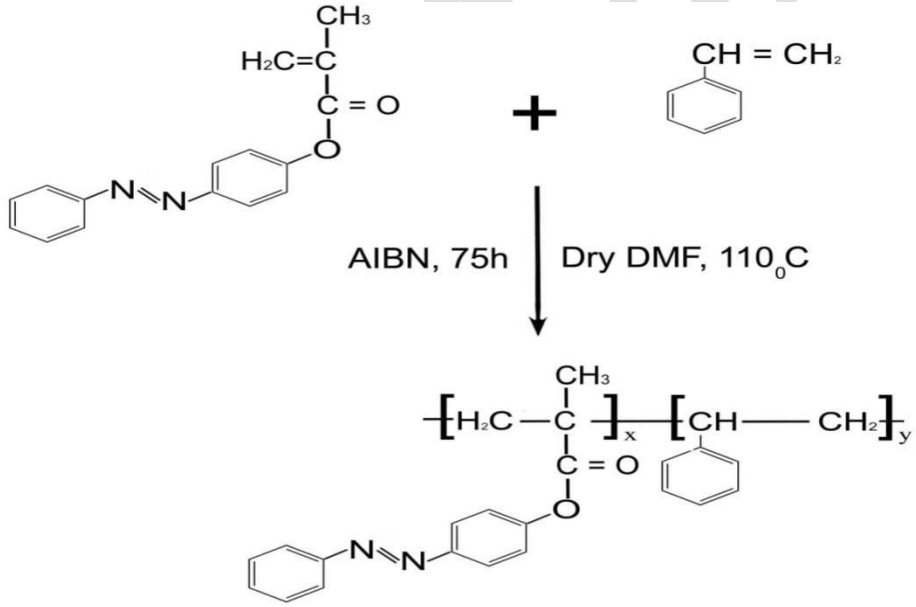
ISSN: 2349-3224 || www.ijaetmas.com || Volume 03 - Issue 07 || July 2016 || PP. 52-55

The synthesis route of 2- methacryloyl-1- (4-azo-1'-phenyl) phenol was given in scheme II.



Scheme - II

Copolymerization of 2-methacnyloyl -1- (4-azo-1'-phenyl) phenol was carried out in dry DMF using AIBN as a radical initiator .The polymer was obtained in moderate yield with good solubility in common organic solvents like chloroform, acetone, THF, DMF, toluene etc. The structure of the polymer was confirmed using FT-IR and NMR spectroscopy. The synthesis route of the polymer was given inScheme – III.



Scheme - III

IV. CONCLUSION:

Non-conjugated photoconducting copolymer, poly(2-methacryloyl-1-(4-azo-1'-phenyl) phenol-co-styrene) was synthesized via radical initiated polymerization of 2-methacryloyl-1-(4-azo-1'-phenyl) phenol and styreneusing solution polymerization technique. The structure of the polymer was confirmed using NMR and FT-IR spectroscopy. The polymer has good photoconducting property. Moreover, Thepolymer can be doped with C_{60} to increase the photocurrent and for quenching of photoluminescence.

ISSN: 2349-3224 || www.ijaetmas.com || Volume 03 - Issue 07 || July 2016 || PP. 52-55

REFERENCES:

[1.] H. J. Bolink, C. Arts, V. V. Krasnikov, G. G. Malliaras, G. Hadziioannou, chem. Mater. 9 (1977), 1407.
[2.] W. Huang, W. L. Yu, H. Meng, J. Pei, S. F. Y. Li , chem.. Mater. 10 (1998), 3340.
[3.] A. C. Arango, S. A. Carter, P. J. Brock, Appl. Phys. Lett. 74 (1999), 1698.
[4.] O. Ostroverkhova, W. E. Moerner, chem. Rev. 104 (2004), 3267.
[5.] T. K. Daubler, L. Kulikovsky, D. Neher, V. Cimrova, J. Hummelen, E. Mecher, R. Bittner,
[6.] K. Meerholz, Proc. Of SPIE 4462 (2002), 206.
[7.] J. Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski, Prog.Polym. Sci. 28 (2003), 1297
[8.] Y. Zhang, H. Sasabea, J. Mater. Chem. 8 (1998), 809.
[9.] E. Mecher, C. Brauchle, H. H. Horhold, J. C. Hummelenc, K. Meerholz, Phys.Chem.Chem.Phys. 1 (1999), 1749.
[10.] M.S. Bratcher, M. S. DeClue, A. Grunnet- Jepsen, D. Wright, B. R. Smith, W. E. Moerner, J. S. Siegel, J. Am.Chem.Soc. 120 (1998), 9680.
[11.] D. Yang, L. Li, C. Wang, Mater. Chem. Phys. 87 (2004), 114.
[12.] S. Shim, M. Suh, S. Suh, X. L. Huang, E. Suh, Polymer 41 (2000), 467.
[13.] V. C. Kishore, R. Dhanya, C. S. Kartha, K. Sreekumar, R. Joseph, J. Appl. Phys. 101 (2007), 0631021.
[14.] S. C. Suh, S. C. Shim, Synth. Met. 114 (2000), 91.
[15.] S.M.Teleb, A. S. Goballa, Spectrochim. Acta. Part A 62 (2005) 140.
[16.] H. Chun, I. K. Moon, D. H. Shin, N. Kim, Chem. Mater. 13 (2001) 2813.
[17.] W.G.Jun, M. J. Cho.D. H. Choi, J. Korean, Phys.Soc. 47 (2005)620.
[18.] L. Angiolini, T. Benelli, L. Giorgini, E. Salatelli, Polymer 46 (2005) 2424.
[19.] M. Toba, Y. Takeoka, M. Rikukawa, K. Sanui, Synth. Met. 152 (2005) 197.
[20.] F. C.Cebeci, E. Sezer, A. S. Sarac, Electrochim. Acta. 52 (2007) 2158.
[21.] L.Angiolini, D.Caretti, l. Giorgini, E. Salatelli, Polymer 42 (2001) 4005.